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Cover Page Footnote
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PULSED BIOSPARGING OF A RESIDUAL FUEL SOURCE EMPLACED AT CFB BORDEN

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1. ABSTRACT

Biosparging enhances both aerobic biodegradation and volatilization, and is commonly applied to residual hydrocarbon source zone remediation. This technology was applied in pulsed mode to a known source of gasoline contamination in order to quantify the extent of remediation achieved in terms of both mass removed and reduction in mass discharge into groundwater. The gasoline source was created by injecting about 40 L of gasoline with 10% ethanol in small volumes from 24 injection points below the water table in 2004. The downgradient plume is still being monitored and the source area was cored in 2007. In 2008, a 3-point biosparge system was operated with an airtight cover to capture and monitor off-gases. Of the hydrocarbons in place, about 80% of pentane, 50% of hexane, but only about 4% of the aromatic hydrocarbons were volatilized and removed. CO_2 and O_2 monitoring in the off-gas confirmed limited biodegradation of hydrocarbons.

2. INTRODUCTION

This paper describes preliminary findings from an investigation of pulsed in situ air sparging applied to treat a small gasoline residual source emplaced in a shallow sand aquifer.

In situ air sparging (IAS) was first used as a treatment technology in the mid-1980s (Bass et al., 2000). Volatilization and O_2-enhanced biodegradation are the mass removal mechanisms. Soil vapor extraction (SVE) is normally used to collect the air sparging gas as it migrates through the vadose zone to the ground surface.

Pulsed air sparging, in which the air sparging is turned on and off (generally based on aquifer response), has been found to be more effective than continuous air sparging in several theoretical (Johnson, 1998 and Ahlfeld et al., 1994) and field studies (Kirtland et al., 2001; and Yang et al., 2005) and so pulsed IAS was employed in this investigation..

No previous evaluation of IAS has made use of a reasonably well known source to quantify the mass removal in terms of the initial mass present. Thomson and Flynn (2000) evaluated SVE in a test cell at CFB Borden and recovered 63% of the available mass of perchloroethylene (PCE). In this study, we are quantifying the mass removed through volatilization and biodegradation from a relatively well-defined source zone using pulsed IAS. The study is also determining the effect of this treatment on downgradient dissolved BTEX concentrations in groundwater.

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3. MATERIALS AND PROCEDURE

3.1 Site Description

The field site is located at Canadian Forces Base (CFB) Borden, 60 km northwest of Toronto, Canada.

The Borden water table aquifer is in a relatively homogeneous, clean, well sorted, fine to medium sand, extending 7 to 8 m below ground surface (bgs). The hydrogeological properties of the Borden sand aquifer have been described by Mackay et al. (1986) and Sudicky et al. (1983). The hydraulic conductivity of core sections taken from within the specific study area ranged from $4.3x10^{-5}$ to $1.5x10^{-4}$ m/s (Yang, 2008). Yang also observed a relatively lower hydraulic conductivity zone ranging from 3.2 to 3.6 m bgs and relatively higher hydraulic conductivity zones at about 2.5 and 4.5 m.

About 40 L of American Petroleum Institute (API) gasoline containing 10% ethanol (a mixture termed E10) was emplaced below the water table in an aquifer volume of 7 to 8 m^3 in October, 2004 (Mocanu, 2007). The E10 residual source is bounded by two rows of sealable sheet piling driven to a depth of 7 m. The resulting dissolved phase plume is monitored extensively using a network of four rows of multilevel monitoring wells, three of which were located downgradient of the E10 residual source. Each row contained seven wells, each with 15 monitoring points.

Sparging in the E10 residual source began on April 28, 2008. At this time no ethanol and little benzene remained in the source. The solubility analog of Raoult's Law (King and Barker, 1999) was used to estimate that about 22 kg or 30 L of gasoline residual remained. Soil cores collected in 2007 (Yang, 2008) suggested that the residual gasoline had not spread more than 0.5 m away from injection wells used for source emplacement and that NAPL residual was still present in the source zone as expected (Figure 1).

3.2 Treatment System

The IAS system consisted of 3 injection points arranged in a line across the source zone. The injection points were driven using a jackhammer to minimize soil disturbance around each point. Each sparge point was 20 cm long and 3 cm in diameter, with four 8-mm holes covered with stainless steel mesh located every 2.5 cm along the length of the housing. Each sparge point was connected to the compressor by 1 cm ID teflon tubing. The top of the screen was set at 5 m bgs; l m below the residual zone (3 to 4 m bgs). Air was injected sequentially into each point at a flow rate of 35 L/min. Pulsed-sparging was used with an on/off cycle of 1.25 h, based on aquifer pressure response times described in section 4.1.

In April, 2008 the water table at this location rose above ground surface, ruling out the use of a standard SVE system to collect sparged gas. Instead, an airtight 7 m x 7 m box was placed over the site to contain soil vapor escaping from the soil surface. Two air pumps were connected in series to an outlet at the top of the box. During sparging, the flow rate out of the box (approximately 100 L/min) was higher than the flow rate into the subsurface. This minimized leaks of sparged gas outside the box.

The treatment system included ports for injecting SF_6 and helium for tracer tests, sample ports for injected and removed air, and two pairs of piezometers inside and outside the box.

Transducers were placed in each piezometer to record water pressure changes during treatment (Figure 2). The system was operated from April 28 to June 23, 2008. The off-gas collection system ran for approximately 280 hours over the 33 days of active sparging. It was operated for a 0.5 hours prior to and for at least 2 hours at the end of each 1.25 h sparging episode. The air injection system operated for a total of 98 hours, less than half the total time the off-gas extraction system was operated.

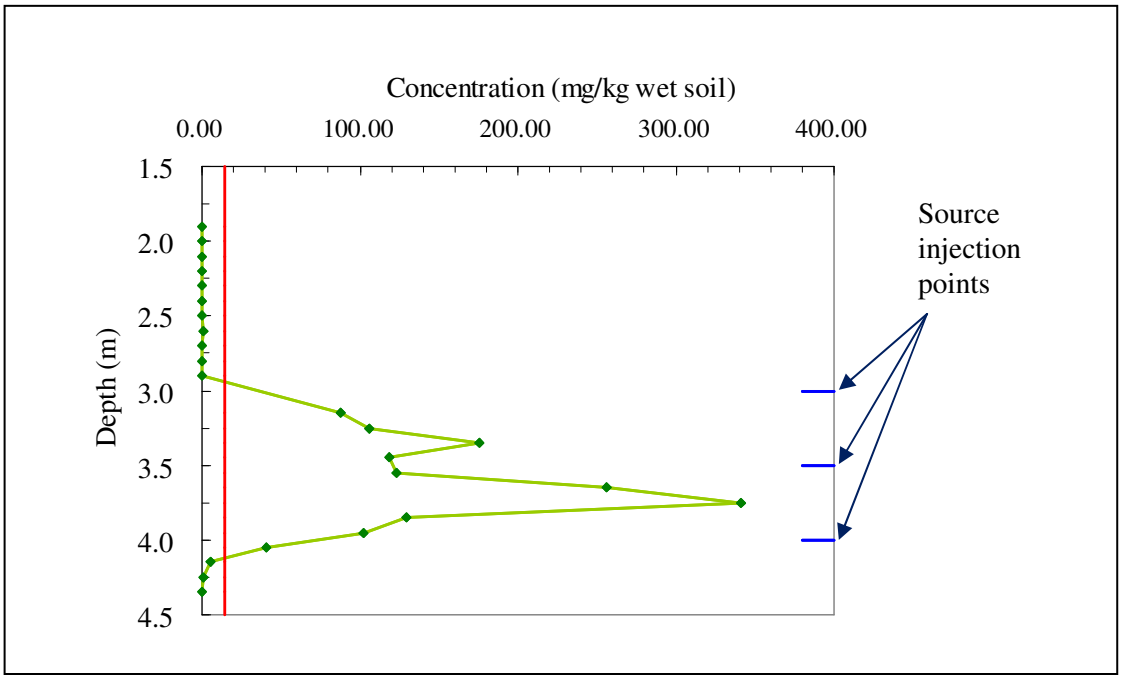

Figure 1. Profile of total aromatic hydrocarbon concentrations (BTEX, trimethylbenzene, and naphthalene) from the center of the E10 residual source zone. The vertical line (17 mg/kg wet soil) indicates the concentration above which residuals are likely present (Yang, 2008).

3.3 Groundwater Sampling

Groundwater samples were collected before (June, 2007) and after (July, 2008) treatment from the multilevel wells in row 2, 3 m downgradient of the gasoline source. The post-treatment sampling was conducted when the groundwater from the last day of treatment reached row 2, based on the estimated advective travel time. This sampling captured groundwater that had been sparged. In July, 2009, row 2 will be re-sampled to establish the longer term groundwater flux reduction due to the pulsed IAS.

Figure 2. Treatment system setup with a dashed white oval around piezometers inside the box, white circles around air sparging points, and a black circle around vapor extraction point. Monitoring row 2 is in the foreground, but covered by the gas collection box.

3.4 Sample Analysis

Off-gas was continuously monitored for hydrocarbon VOCs, including benzene, toluene, ethylbenzene, m/p-xylene, o-xylene (termed BTEX), pentane, hexane, and total petroleum hydrocarbons ranging from C_6 to C_{10} (termed TPH–F1), using a mini-RAE 2000 photo-ionization detector (PID). Off-gas samples were also collected at regular intervals for hydrocarbon analysis using a Hewlett Packard 5890 gas chromatograph (GC). Groundwater samples were analyzed for BTEX, trimethylbenzenes isomers, and naphthalene using the same equipment. Off-gas samples were also analyzed for O_2 and CO_2 using a Fisher/Hamilton Model 29 gas partitioner or a GOW-MAC (series 350 GP) GC. The latter equipment was only used to determine CO_2.

Helium tracer tests were conducted throughout the treatment period to determine how much of the injected air was recaptured in the off-gas collection system. These tracer data were inconclusive because of helium loss prior to injection. However, visual evidence (lack of bubbles on the standing water) indicated the collection box captured essentially all sparged hydrocarbons.

4. DATA AND ANALYSIS

4.1 Water Pressure Fluctuations

Pressure transducer data indicated that the water pressure was maximized within about 5 minutes of starting the air sparging system and then quickly dropped off (Figure 3). Based on this response, the pulse sparge cycle time was set at 1.25 hour.

The strongest pressure responses were observed in P1, the deeper transducer closest to the sparging point screen and in P2, the other point within the gas collection box. The transducer data inside the box indicated an above-ground piezometric surface, which was consistent with visual observations of groundwater mounding just outside the gas collection box.

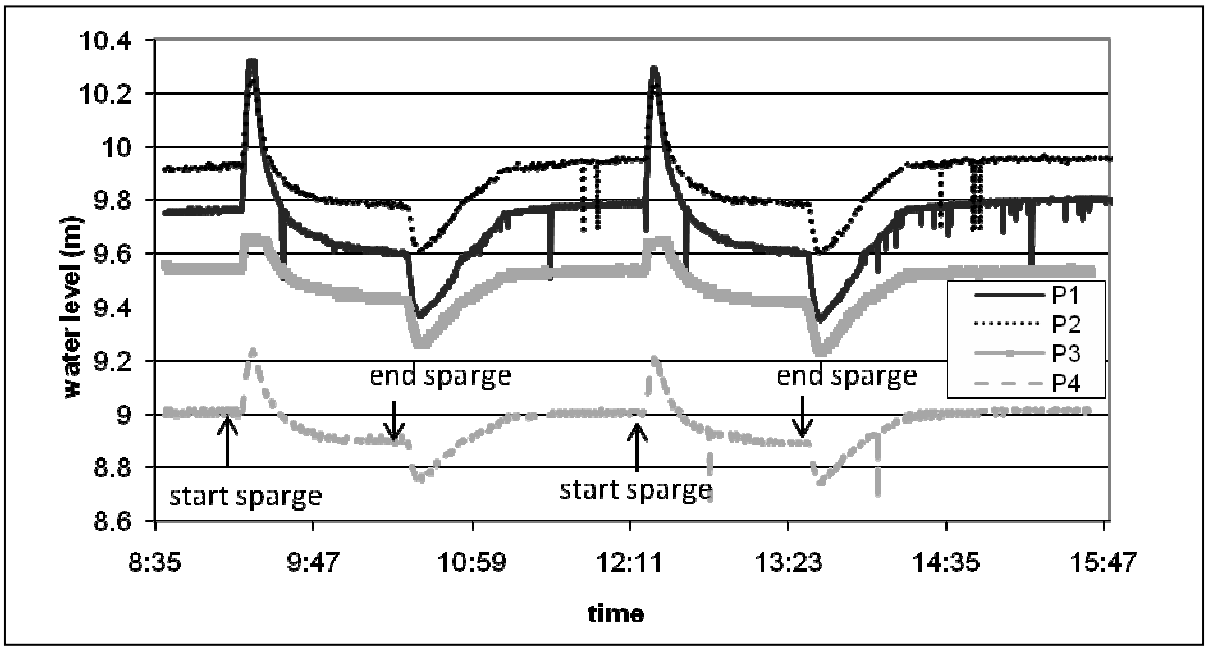

Figure 3. April 30 transducer data showing aquifer response to pulsed sparging. P1 and P2 are inside the box; and P3 and P4 are outside. P1 and P3 are deeper. The ground surface elevation was set at 10 m.

4.2 Off-Gas Data

The hydrocarbon gas concentrations peaked in the first 16 hours of pulsed IAS, when the central sparging point was used, and then declined thereafter (Figure 4). The second concentration peak at approximately 100 hours corresponds to a switch to the second air injection point. The third injection point was used only briefly due to equipment issues at 140 hours and then again from 230-240 hours, but little hydrocarbon gas was recovered.

The PID data do not show any short duration peaks that would have been missed by the sampling schedule adopted. They confirm the representativeness of the samples collected for GC analysis. The PID gives a total VOC concentration and is used to define trends in individual compounds and the F1 hydrocarbon fraction within the GC gas concentration data.

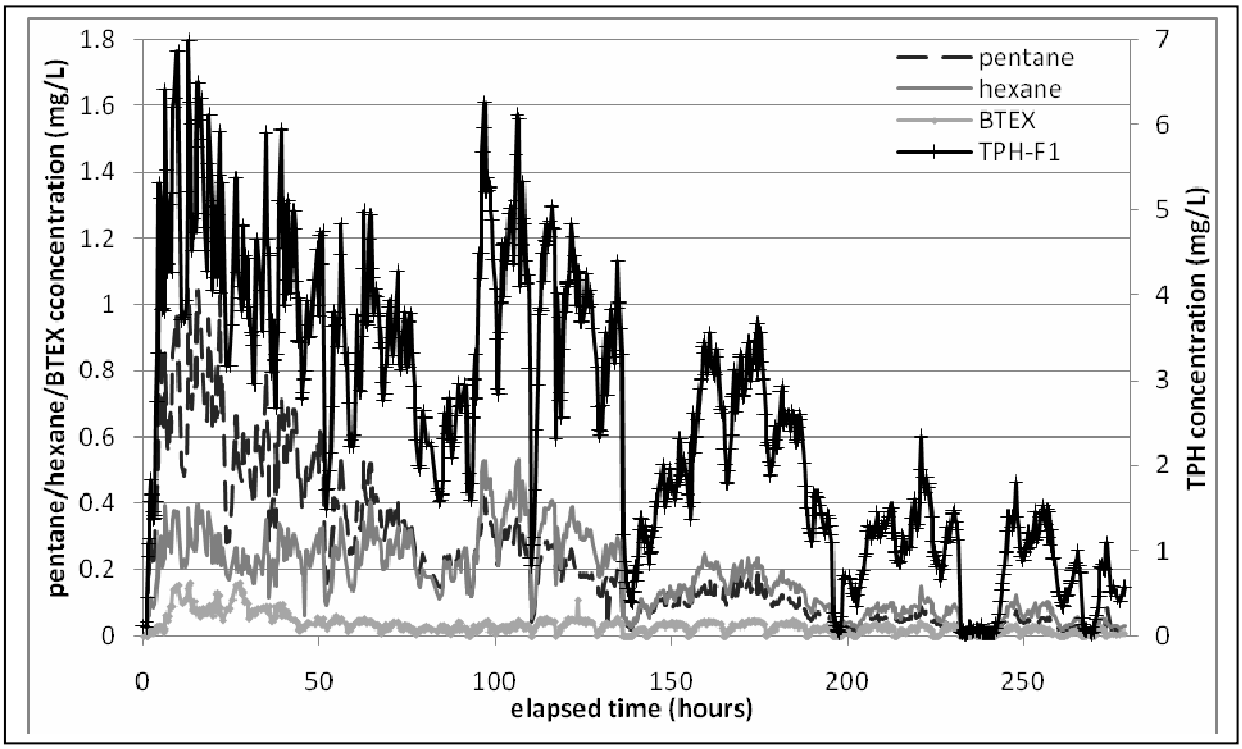

Figure 4. GC concentrations over the course of sparging. Note that the elapsed time represents the time of active soil gas extraction system operation and not the duration of the investigation.

Off-gas concentrations declined sufficiently for the system to be turned off after 280 hours of operation. Sparging of the most volatile constituents (pentane and hexane, with vapor pressures of 526 and 150 mm Hg, respectively) far exceeded sparging removal of the target monoaromatics (average 13 mm Hg) (data from Montgomery, 2000). Approximately 80% of the pentane and 50% of the hexane present in the residual gasoline were recovered in the gas collection system. Only about 4% of the TEX was recovered, and benzene was not detected in the off-gas.

CO_2 concentrations increased and O_2 concentrations decreased slightly from baseline concentrations (Lambert, 2008). This confirms that some aerobic biodegradation had occurred, but quantifying the extent is still underway.

4.3 Downgradient Groundwater Data

Post-sparging groundwater collected in 2008 indicate a significant decrease in the average concentration and so in mass flux at row 2. The decrease was 27%, 92%, 65%, 6%, and 5% for B, T, E, p/m-X, and o-X, respectively. However, the hydrocarbon mass fluxes were already declining and so it is not yet clear how much of this reduction can be attributed to the sparging and if significant decreases will continue. Groundwater sampling will be repeated in 2009 to determine if the remediation activity has produced a long-term decrease in groundwater mass flux.

5. SUMMARY

Pulsed IAS and an off-gas collection system were used to remediate approximately 30 L of residual gasoline below the water table in the Borden sand aquifer. While more than 50% of the more volatile hydrocarbons, pentane and hexane, were recovered in the off-gas, less than 5% of the TEX were removed during the 98 hours of pulsed IAS conducted over two months. Sparging was discontinued due to minimal hydrocarbon recovery. It appears unlikely that additional TEX would be recovered unless the sparging system was altered (e.g., moving the sparging wells). Enhanced CO_2 and depressed O_2 concentrations in the off-gas indicate that oxygen added to the subsurface supported in situ biodegradation. Further sparging may have contributed to continued aerobic biodegradation of hydrocarbons.

The poor removal of TEX in the off-gas demonstrates the difficulty of efficiently sparging even a small, well-defined residual gasoline source in a rather homogeneous sand aquifer. Evaluation of the ultimate benefit of this short-duration, pulsed biosparging, specifically reduction of the dissolved hydrocarbon flux emanating from the remaining residual gasoline, continues with additional groundwater sampling planned for 2009.

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